

CLAIMS

1. A process for producing higher molecular weight hydrocarbon compounds or oxygenates from a gas comprising methane, said process comprising:
generating synthesis gas ("syngas") comprising carbon monoxide and hydrogen by reaction of a gas comprising methane with steam and/or an oxidant gas comprising oxygen;
producing higher molecular weight hydrocarbon compounds or oxygenates in a syngas conversion process;
removing offgas comprising unreacted hydrogen and unreacted carbon monoxide from said syngas conversion process; and
separating unreacted hydrogen from said offgas or from a gas derived therefrom to produce separated hydrogen product,
wherein unreacted hydrogen is separated in a cryogenic separation process to produce separated hydrogen product that is substantially free of unreacted carbon monoxide and a first cryogenic liquid comprising unreacted carbon monoxide.
2. A process as claimed in Claim 1 wherein the cryogenic separation process is a liquid methane wash.
3. A process as claimed in Claim 1 or Claim 2 wherein higher molecular weight hydrocarbon compounds are produced, said process further comprising using separated hydrogen product for hydrogenation of a fraction of said higher molecular weight hydrocarbon compounds to produce liquid hydrocarbon compounds.
4. A process as claimed in Claim 3 wherein said separated hydrogen product is used in the hydrogenation of said hydrocarbon fraction without purification.
5. A process as claimed in any of Claims 1 to 4 further comprising separating unreacted carbon monoxide from said first cryogenic liquid or from a cryogenic

liquid derived therefrom in a cryogenic distillation column to produce separated carbon monoxide product and substantially carbon monoxide-free cryogenic liquid.

6. A process as claimed in Claim 5 further comprising recycling separated carbon monoxide product for conversion into higher molecular weight hydrocarbon compounds or oxygenates.

7. A process as claimed in Claim 5 or Claim 6 wherein said first cryogenic liquid further comprises argon, said process further comprising removing at least one argon-enriched stream from a location in the region of high argon concentration in the cryogenic distillation column.

8. A process as claimed in any of Claims 5 to 7 wherein the substantially carbon monoxide-free cryogen liquid is substantially pure liquid methane, said process further comprising recycling a vaporised portion of said substantially pure liquid methane for conversion into syngas.

9. A process as claimed in any of Claims 1 to 8 wherein said offgas further comprises helium, said process further comprising separating helium from said separated hydrogen product using a membrane separation system.

10. A process as claimed in any of Claims 1 to 9 wherein said offgas further comprises low molecular weight hydrocarbon compounds, said process further comprising:

cooling said offgas or a gas derived therefrom to condense said low molecular weight hydrocarbon compounds to produce liquefied petroleum gas ("LPG") and removing said LPG to produce substantially LPG-free offgas;

cooling and at least partially condensing said substantially LPG-free offgas to produce partially condensed substantially LPG-free offgas; and

separating unreacted hydrogen from a vapour portion of said partially condensed substantially LPG-free offgas in said cryogenic separation process to produce said separated hydrogen product and said first cryogenic liquid.

11. A process as claimed in Claim 10 wherein unreacted hydrogen is present in said first cryogenic liquid, said process further comprising separating unreacted hydrogen from said first cryogenic liquid or a cryogenic liquid derived therefrom in a further cryogenic separation process to produce separated hydrogen fuel by-product and a second cryogenic liquid comprising unreacted carbon monoxide.

12. A process as claimed in Claim 11 wherein the further cryogenic separation process is a liquid methane wash.

13. A process as claimed in Claim 11 or Claim 12 wherein said offgas further comprises helium and wherein separated hydrogen product is recycled for conversion into higher molecular weight hydrocarbon compounds, said process further comprising removing a portion of said separated hydrogen product once the concentration of the helium in the separated hydrogen product is between from 1 mol % to 20 mol %.

14. A process as claimed in Claim 13 wherein said portion is adjusted in flowrate so that the helium concentration reaches the required concentration.

15. A process as claimed in any of Claims 1 to 14 further comprising at least partially vaporising liquid nitrogen ("LIN") to provide refrigeration duty to keep the process in heat balance.

16. A process as claimed in any of Claims 1 to 15 wherein the oxidant gas is oxygen with a purity below 99 mol % produced in an integrated cryogenic air separation process, said LIN being produced in said air separation process.

17. A process as claimed in any of Claims 1 to 16 wherein separated hydrogen product is recycled for conversion into higher molecular weight hydrocarbon compounds.

18. A process as claimed in any of Claims 1 to 17 wherein said syngas is generated by partially oxidizing natural gas with oxygen and by reforming natural gas with steam.

19. A process as claimed in any of Claims 1 to 18 wherein said syngas conversion process is a Fischer-Tropsch ("FT") process.

20. Apparatus for the production of higher molecular weight hydrocarbon compounds or oxygenates from a gas comprising methane according to the process as defined by Claim 1, said apparatus comprising:

a syngas generation system for generating syngas comprising carbon monoxide and hydrogen by reaction of a gas comprising methane with steam and/or an oxidant gas comprising oxygen;

a syngas conversion system for converting syngas into higher molecular weight hydrocarbon compounds or oxygenates and producing offgas comprising unreacted hydrogen and unreacted carbon monoxide; and

a cryogen separation system for separating unreacted hydrogen from said offgas or a gas derived therefrom to produce separated hydrogen product that is substantially free of unreacted carbon monoxide and a first cryogenic liquid comprising unreacted carbon monoxide.

21. Apparatus as claimed in Claim 20 wherein the cryogenic separation system is a first liquid methane wash column.

22. Apparatus as claimed in Claim 20 or Claim 21 producing higher molecular weight hydrocarbon compounds, said apparatus further comprising a hydrogenation system for hydrogenating a fraction of said higher molecular weight

hydrocarbon compounds using separated hydrogen product to produce liquid hydrocarbon compounds.

23. Apparatus as claimed in any of Claims 20 to 22 further comprising a cryogenic distillation column for separating unreacted carbon monoxide from said first cryogenic liquid or from a cryogenic liquid derived therefrom to produce separated carbon monoxide product and substantially carbon monoxide-free cryogenic liquid.

24. Apparatus as claimed in Claim 23 further comprising conduit means for feeding separated carbon monoxide product from said cryogenic distillation column to said syngas conversion system.

25. Apparatus as claimed in Claim 23 or Claim 24 further comprising conduit means for removing an argon-enriched stream from a location in the region of high argon concentration in said cryogenic distillation column.

26. Apparatus as claimed in any of Claims 23 to 25 wherein said substantially carbon monoxide-free cryogenic liquid is substantially pure liquid methane, said apparatus further comprising conduit means for feeding substantially pure liquid methane from said cryogenic distillation column to said syngas generation system.

27. Apparatus as claimed in any of Claims 20 to 26 wherein the offgas further comprises helium, said apparatus further comprising a membrane separation system for removing helium from separated hydrogen product.

28. Apparatus as claimed in any of Claims 20 to 27 wherein unreacted hydrogen is present in said first cryogenic liquid, said apparatus further comprising a second liquid methane wash column in which unreacted hydrogen is separated from said first cryogenic liquid or a cryogenic liquid derived therefrom to produce

separated hydrogen fuel by-product and a second cryogenic liquid comprising unreacted carbon monoxide.

29. Apparatus as claimed in Claim 28 wherein said offgas further comprises helium and wherein separated hydrogen product is recycled for conversion into higher molecular weight hydrocarbon compounds or oxygenates, said apparatus further comprising conduit means for removing a portion of said separated hydrogen product having a concentration of helium between from 1 mol % to 20 mol %.

30. Apparatus as claimed in any of Claims 20 to 29 wherein the syngas generation system comprises a partial oxidation ("POX") reactor and an enhanced heat transfer reformer ("EHTR").

31. Apparatus as claimed in any one Claims 20 to 30 wherein the syngas conversion system comprises at least one FT reactor.

32. A process substantially as hereinbefore described with reference to the accompanying drawings in Figures 2 to 4.

33. Apparatus substantially as hereinbefore described with reference to the accompanying drawings in Figures 2 to 4.

INTERNATIONAL SEARCH REPORT

Application No
PCT/GB 03/03403

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 4 782 096 A (BANQUY DAVID) 1 November 1988 (1988-11-01) claims 1,15 column 9, line 61 - line 65 figures 1-5 | 1,2,5, 18,20, 21,23,30 |
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| X A | US 5 173 513 A (PINTO ALWYN) 22 December 1992 (1992-12-22) claim 1 column 12, line 16 - line 21 | 20 1,5,7-9 |
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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